Intensified thermocatalytic CO_2 conversion to chemicals and fuels

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CO_2 hydrogenation to chemicals and fuels has the potential to reduce CO_2 emissions while displacing fossil resources. Yet, the chemical inertness of CO_2 makes its direct conversion to C_{2+} hydrocarbon products fundamentally challenging, requiring C_1 intermediates such as CO or methanol [1]. This keynote lecture explores both routes for process-intensified CO_2 conversion: the CO-mediated via integration of reverse water–gas shift (RWGS) with Fischer-Tropsch synthesis (FTS), and the methanol-mediated conversion to hydrocarbons.

The first part focuses on iron- and cobalt-based catalysts for CO_2/CO/H_2 conversion to C_{2+} hydrocarbons. Iron catalysts are intrinsically bifunctional, catalyzing both RWGS and FTS, and therefore offer the possibility of direct CO_2 conversion in a single reactor. However, exploiting this bifunctionality requires balancing CO formation and consumption rates, hydrocarbon chain growth, and methane suppression. Using carbon-supported potassium-promoted iron-based catalysts, I will show how catalyst characteristics and process parameters such as CO_2 conversion influence reaction pathways and overall performance [2,3]. In contrast, cobalt catalysts predominantly hydrogenate CO_2 to methane, motivating a different approach to process integration. Using a conventional titania-supported metallic cobalt catalyst, I will showcase the boundary conditions under which CO_2 behaves as an inert component, and those under which it becomes reactive, in CO_2/CO/H_2 feeds entering a cobalt-catalyzed FTS reactor [4]. These results provide insight into when conventional staged configurations are necessary and when more integrated reactor concepts may be feasible.

The second part addresses methanol-mediated conversion to light olefins, focusing on the methanol-to-olefins (MTO) process. Using a series of isomorphically substituted AEI-type zeotypes (MAPO-18, M = Si, Mg, Co, Zn), I will demonstrate how framework composition and acidity influence MTO performance under CO_2/CO/H_2 co-feeds [5]. In particular, I will discuss how H_2 promotes catalyst activity but can also hydrogenate olefins, while CO suppresses this undesired reaction over Brønsted acid sites. I will discuss the challenges of bridging conventional MTO chemistry with oxygenate-mediated CO_x conversion and provide an assessment of methanol, dimethyl ether, and ketene as potential oxygenate intermediates [6].

Together, these studies illustrate how reaction engineering, catalyst design, reactor and process integration must be considered collectively to unlock efficient and selective conversion of CO_2 to chemicals and fuels.

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